Effect of specially formulated graphite on the thermo-mechanical properties of Al_2O_3-C slide gate plate refractory

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CERTIFICATE

*This is to certify that the thesis entitled, "**Effect of specially formulated graphite on the thermo-mechanical properties of Al_2O_3-C slide gate plate refractory**",*

submitted by Mr. Santosh Kumar Patra carried out in National Institute of Technology, Rourkela, in partial fulfillment of the requirements for the award of Bachelor of Technology Degree in Ceramic Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree or diploma.

I wish him all the success for his future.

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Abbreviation

AP-Apparent Porosity

BD-Bulk Density

HMOR-Hot Modulus of Rupture

CCS-Cold Crushing Strength

OI-Oxidation index

SFG-Specially formulated graphite

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ABSTRACT

In this study, a different approach has been followed to improve the thermo-mechanical properties and oxidation resistance of Al_2O_3-C slide gate plate refractories. In the present work, specially formulated graphite (SFG) was used as carbon source to partially replace flaky graphite by the SFG in Al_2O_3–C refractories in order to study the effect of its addition on the mechanical and thermo-mechanical properties. Al_2O_3-C refractory batches fortified with various fractions of SFG were prepared on a pilot plant scale, and their thermo-mechanical properties were studied. Bulk density, apparent porosity, cold crushing strength, hot modulus of rupture and oxidation resistance were the properties studied across a series of batches. The new compositions exhibited excellent hot strength and oxidation resistance. Microstructural observation indicated easy formation of nanostructured whiskers are fiber thus improving the hot strength and oxidation resistance. The positive effect of addition of specially formulated graphite to Al_2O_3-C refractory has been well-established in this study. A huge potential exists for future commercial exploitation of the concepts embodied in this work.

Chapter 1

INTRODUCTION

1.1 Introduction

Refractories, a key input of iron and steel making, assume ever increasing role due to high stress on production of high quality sophisticated steels, steal making alone accounts for the consumption of nearly 70% of total refractory produced [1]. Refractory is defined by ASTM C71 as "nonmetallic inorganic materials having chemical and physical properties that make them applicable for structures or as components of systems that are exposed to environments above 1000°F (538°C)" [2]. Refractories have very good mechanical properties at high temperature as well as at low temperature. They have good corrosion and erosion resistance to molten slag, metals and hot gases. Due to good thermo-mechanical and thermo-chemical properties refractory materials are used in various high temperature processes, including iron and steel making, non-ferrous metal processing, cement, glass, chemical industries etc. They are normally used in high temperature furnaces, kilns, boilers, incinerators etc.

Many scientific and technological inventions and developments would not have been possible without refractory materials. Without the use of refractory manufacturing of any metal is almost impossible. Iron and steel industries are the main consumers of refractory. So, the refractory production has to be in sync with the demand of iron and steel industries. Better manufacturing and application environment is demanding a new generation of refractory material with improved properties, performance and life with eco-friendliness.

Refractories can be classified into three groups based on their raw materials:

1. Acidic (zircon, fireclay and silica)
2. Basic(dolomite, magnesite, magnesia-carbon, alumina/magnesia-carbon, chrome-magnesite and magnesite-chrome)
3. Neutral (alumina, chromite, silicon carbide, carbon and mullite)

1.2 Materials system for slide gate plate

Slide gate plate valves are formed from heat and erosion resistant refractory materials, such as aluminium oxide, magnesium oxide, alumina-carbon, magnesia- carbon, and zirconium oxide among others. The heat and erosion resistance properties of such materials, such plates are eventually erode, corrode or become plugged to a point that the plates are no longer withstand

high temperature. Exchange of the slide gate takes place after a certain number of heats. Since its inception slide gate, to meet the development needs of the steelmaking process, skateboards material has been constantly improved. There are typical skateboard Materials are Al_2O_3-C quality, Al_2O_3-ZrO_2-C quality, MgO quality, MgO-Al_2O_3 quality, MgO-Al_2O_3-C quality.

The raw materials play a vital role in the performance and life of the refractories. Several research works had been carried out to find out the effect of different raw materials based on purity, crystallite size, porosity and other parameters of different raw materials on the final properties of Al_2O_3-C refractories. The main raw materials are tabular alumina, graphite, carbon black, antioxidants and binder like resin.

Graphite has non-wetting property which improves the corrosion resistance because the slag can't penetrate the refractories. The thermal shock resistance of the Al_2O_3-C system is very good, but it is susceptible to oxidation. Antioxidants prevent oxidation of carbon and improve high temperature strength by the formation of carbides. If carbon leaves the system then slag can penetrate easily into the refractories which will ultimately degrade the strength of the refractories.

Carbon in refractories has the advantages of non-wettability by molten slag, high thermal conductivity and low thermal expansion. All of these features give rise to Al_2O_3–C refractories with excellent physical and chemical characteristics at elevated temperature, such as high hot strength, and good resistance to both thermal shock and slag. Therefore, Al_2O_3–C refractories can withstand long lasting and repetitive chemical corrosion and mechanical attack coming from both molten steel and slag. Nowadays, Al_2O_3–C refractories are widely used as functional elements like nozzles, well blocks, sliding gate plates and stoppers in the continuous casting process of steel production. The function of these refractories is to control flow field and velocity, decrease the addition of impurity and prevent the oxidation of molten steel.

Al_2O_3–C refractories typically consist of corundum aggregate (larger than 0.088 mm) and the fine powder of matrix (smaller than 0.088 mm). The matrix usually contains corundum powder, graphite, anti-oxidant, binders and so on. The role of the matrix is to interlink coarser particles of the material. So the properties of the matrix could determine the density and mechanical strength of the refractories at room and high temperature. However, the matrix consisting of fine powder is often porous, fragile and is easily eroded. When Al_2O_3–C refractories are attacked by molten

liquids, the cracking and spalling occurs first in the matrix and ultimately deteriorates the comprehensive properties of the refractories. In order to enhance the properties of the matrix, metals are added into the matrix as anti-oxidants because these metals can form ceramic bonding phases of SiC. The ceramic bonding phases, often taking on one dimensional structure, would reinforce the matrix and enhance the hot strength of Al_2O_3–C refractories through tightly interlinking the particle of corundum and graphite.

In most of the literature, it was found that the variation in different alumina aggregates, either brown fused, white fused or tabular alumina influence the physical, thermo-mechanical as well as thermo-chemical properties[3]. Most of the literatures have been focusing the properties and performance of alumina-carbon refractories on the basis of different alumina aggregates like white fused alumina (WFA) or brown fused alumina (BFA) or tabular alumina (TA). Very few literatures have reported the combined effect of alumina aggregates (type and amount) on the properties of the Al_2O_3-C refractories. The present research work aims to study the effect in physical properties like apparent porosity (AP) and bulk density (BD), mechanical properties like hot modulus of rupture (HMOR), cold crushing strength (CCS), and modulus of elasticity (MOE) and thermo-chemical properties like oxidation resistance and of Al_2O_3-C refractory by varying the percentage of specially formulated graphite.

1.3 Slide gate plate refractory

Slide gate plate is one of the most important refractory for continuous casting of steel and it is used for precise flow control and a safety operation. Slide gate plate are used in ladle, tundish, where it is expose to sudden thermal shock, physical abrasion by molten hot metal and slag. Therefore the slide gate plate must have good resistance to both thermal shock and corrosion. The capacity and cost of steel making depends upon the structure of slide gate plate refractories. According to the requirement of steel production, slide gate plate can be made of alumina/graphite or magnesia/graphite. Alumina/carbon refractories are used widely in recent years so as to prevent fuming due to pitch, which has conventionally been used in the plate, in consideration of higher durability and service environment. The alumina/graphite has the disadvantage that it is easily corroded by “Ca” treated steel and high oxygen contacts. The basic materials have good corrosion resistance as compare to neutral metals, and depend upon the steel grade. But the neutral metals have less thermal spalling resistance due to high thermal expansion coefficient.

Alumina/zirconia/carbon slide plates are generally used in ternium siderar steel ladles. In steel making process when high-temperature fluid such as molten metal flow through the nozzle of slide gate plate, a large temperature difference occurs between the inside and outer part which is away from the nozzle hole, and thus some kind of material constituting these portions are frequently damaged by thermal shock. Therefore, refractory material which has high resistance against thermal shock, but relatively low fineness has been used for the gate plate device. [4]

Slide gate plate of a zirconia-based material, ~~are~~ lack in stability in spalling resistance and therefor, does not promise satisfactory durability of the slide gate nozzle for receiving a melt of special steel particularly molten steel deoxidized with "Ca" alloy.

Al_2O_3-C refractories are widely used in steel casting operations. Basic representatives of this refractory product group are the so called functional components, like submerged entry nozzles, mono-block stoppers and ladle shrouds, which are used in the continuous casting of steel.

Fig 1.1: slide gate plate

Chapter 2

LITERATURE REVIEW

2.1 Basics of Al_2O_3-C slide gate plate refractories

In alumina carbon slide gate plate refractories the main raw material is used as alumina and less amount of carbon. But the problem was Oxidation of carbon at temperature above 600°C which leads to the deterioration of properties in refractories i.e. increase of porosity, decrease of strength and corrosion resistance. And Erosion (chemical or physical) by penetration of molten metal or slag in the pores or due to the dissolution of alumina by slag or the oxidation of carbon by iron oxide in liquid slag and ambient gas. So to avoid that some additives and antioxidants are added to reduce the oxidation and to increase the thermochemical strength of the slide plate refractories.

The raw materials used for Al_2O_3-C slide gate plate refractory manufacturing are the aggregates consisting of tabular alumina, flaky graphite, carbon black, binder (phenolic resins, hexamine) and antioxidants (metallic Si and/or Al powder, or nonmetallic SiC).

Different alumina aggregates, in general fused and sintered alumina have been used for the processing of the alumina-carbon refractories. White fused alumina (WFA) and brown fused alumina (BFA) were coming under the fused alumina category and tabular alumina (TA) is under sintered category. It has been reported that the properties of Al_2O_3-C refractory is influenced by the type of alumina aggregates.

2.1.1 Role of graphite

Flaky graphite is used as a source of carbon in the manufacturing of Al_2O_3-C refractories due to its following properties:-

- High melting temperature
- High thermal conductivity
- Low thermal expansion coefficient
- High thermal shock resistance
- Low friction and hence good compressibility character
- Low wettability to molten slag and hence better corrosion or erosion resistance
- Good oxidation resistance. It starts to be oxidized in oxidizing atmosphere at (500°C).

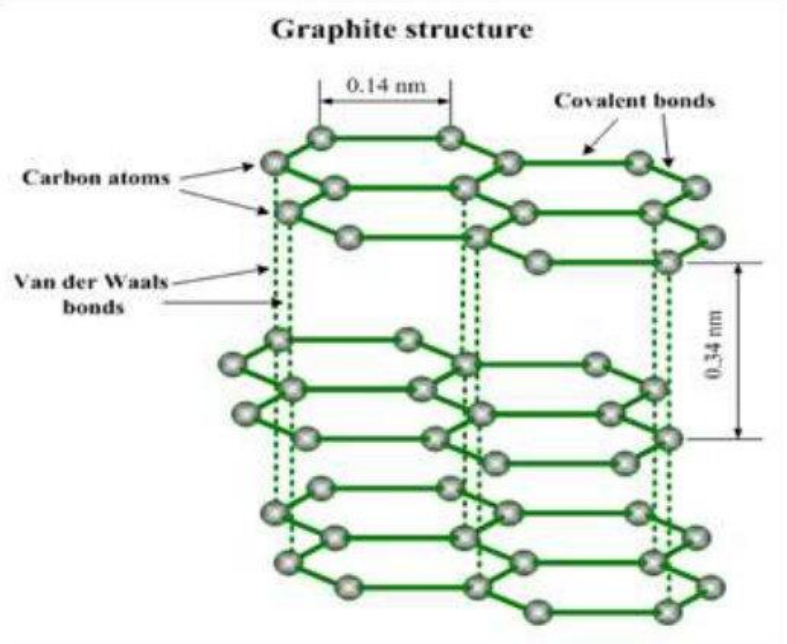

Fig.2.1: Crystal structure of graphite

In Al_2O_3-C slide gate plate, carbon plays a very important role by providing non-wetting nature to the refractory. Graphite is used as the carbon source because among different commercial sources of carbon, graphite shows the highest oxidation resistance. Carbon gets oxidized in oxidizing atmosphere which results a porous structure with very poor strength. So, resistance against oxidation is very important for the carbon source. Due to the flaky nature of graphite it imparts higher thermal conductivity and lower thermal expansion, resulting in very high thermal shock resistance. Along with the increase of the graphite content the compressibility increases during pressing and results in a decrease in the porosity. Fine graphite particles are more effective to improve the corrosion resistance of refractory. The strength of Al_2O_3-C brick particularly during heat treatment has also been reduced by the bigger particle size of graphite. Purity of graphite is also an important factor. Impurities react with Al_2O_3 and form low melting phase which results in lower corrosion resistance and also lower hot strength.

Graphite's role in Al_2O_3-C bricks can be summarized as –

i. Graphite covers the spaces in between alumina grains and fills the porous brick structure.
ii. Graphite prevents the slag penetration into the slide gate plate due to high wetting angle between slag and graphite.

iii. At higher temperature alumina reacts with carbon to form aluminum metal and carbon di oxide, Some antioxidant like "Si" metal is added to prevent the oxidation of carbon but in the later stage silicon reacts with carbon to form silicon carbide which gives strength to the material.

iv. Graphite improves the thermo–mechanical properties and spalling resistance of the brick because of its high thermal conductivity and low thermal expansion. The size of graphite has also a great role in improving the abrasion, corrosion and oxidation resistance of Al_2O_3-C refractory.

2.1.2 Role of fused silica

Fused silica is used as refractory aggregates in Al_2O_3-C refractory in order to reduce the thermal expansion coefficient of Al_2O_3-C refractory. It also reacts with the alumina at high temperature and forms mullite which provides better interlocking structure and imparts better high temperature strength. The amorphous nature of fused silica has a disadvantage of forming low melting compound with the other aggregates of the refractory, which leads to deterioration of high temperature properties of the alumina-carbon refractory.

2.1.3 Role of binder

The main role of binder is to provide green strength to ceramic bodies. In addition to this cohesive action, selection of binders usually involves consideration accompanying characteristics of the aggregates. Generally Phenolic resins have been used as binder for the Al_2O_3-C slide gate plate refractories as they can be pyrolysed during coking to achieve a high carbon yield about 55-65% of their solid content as carbon. The phenolic resin provides better carbon bonding & compatibility with other carbonaceous materials but it has the disadvantage of lower oxidation resistance than other binders like pitch.

Because of flaky and non-wetting characteristics of graphite, it is very difficult to produce a dense brick without any strong binder. In the early days pitch was used as binder for Al_2O_3-C refractory. But during operation pitch releases large amounts of volatile matters, which are very toxic due to their high content of polycrystalline aromatic compound (PAC) like benzo alpha-pyrenes. Also to use pitch hot pressing of the mixture was necessary. So, resin was found to be the best binder for Al_2O_3-C refractories because of these following properties:-

i. Resin contains high amount of fixed carbon which gives strong bonding property.
ii. Because of its thermosetting nature resin possesses high dry strength.
iii. It produces less hazardous gas than tar/ pitch.
iv. At curing temperature (~200^{o}C) resin polymerizes which gives isotropic inter-locking structure.
v. Cold crushing strength (CCS) increases with the increase of resin content.

The desired viscosity of resin should be around 8000 cps, which ensures proper mixing of the other raw materials. Viscosity of resin is quite sensitive to temperature which increases with decrease in temperature. In winter viscosity of resin increases, which causes low dispersion of ingredients in the mixer machine. Whereas in summer due to high temperature viscosity decreases which gives less strength in the green body and ceates lamination. Powder novalac resin is normally used to overcome from this type of difficulty [5]. Compressibility during pressing improves with the increase in resin content and consequently the CCS of the tempered samples increase. The resol type resin is best as binder among various resin types. Because of is lower viscosity and lower content of volatile species the samples containing resol had the lowest porosity after heating at high temperature.

2.1.4 Role of antioxidant

The antioxidants are used as additives to the Al_2O_3–C refractories, in order to improve their poor oxidation resistance as well as for mechanical reinforcement. Usually fine metallic powders (Si, Al) in the range of up to 150μm are used as antioxidants, as well as carbides (SiC, B_4C, Al_4SiC_4, $Al_8B_4C_7$) and boron containing oxides (fluxes) in the range of up to 100μm. The improvement of the oxidation resistance is being achieved with respect to the following mechanisms: the antioxidants react with the $CO_{(g)}$ of the surrounding atmosphere forming $SiO_{(g)}$ (in case of adding Si or SiC) and reducing $CO_{(g)}$ to $C_{(s)}$, thus suppressing oxidation loss of carbon. The formed $SiO_{(g)}$ further reacts with $CO_{(g)}$ and deposits a thin protective layer of $SiO_{2(s)}$ on the graphite surface, thus reducing the active sites. Furthermore, these reactions are accompanied with a volume expansion, which can seal the pores of the refractory [6]. This effect is being utilized in the case of using boron containing compounds as antioxidants, whereby a glass phase formation is seals the pores of the refractory [7]. In many cases, various antioxidants are being used together for further improvement of the refractories performance.

In alumina–carbon refractories in the context of oxidation protection of carbon bonds. The function of antioxidant is given as below:-

- They themselves melt or form low melting glassy phase and coats the carbon bonds to protect them from being oxidized.
- Get oxidized and reduce the partial pressure of oxygen available to oxidize the carbon bonds.

However, the addition of antioxidants should be optimized to make a balance between the properties of oxidation and corrosion resistance. Generally, metallic silicon, aluminium powder or nonmetallic carbides such as SiC were used as antioxidants or (additives) in the Al_2O_3-C refractories to improve the physical and thermo-mechanical properties.

2.2 Effect of additives on Al_2O_3-C slide gate plate refractory

Javadpour et al. [8] have studied the effect of Al and Si additions on the properties and microstructure of Al_2O_3-C refractories. It has been observed that the strength increases and porosity decreases with increase in the Al as well as Si content in the samples. This improvement was due to the formation Al_4C_3 and AlN phases in the Al containing samples and SiC formation in case of Si containing samples. It has also been reported that the improvement in the properties are sensitive to firing temperature in case of Al additive but not for Si additive. For example the strength was found to decrease with increase in firing temperature in case of Al containing sample and the same was found to increase in Si containing samples. The lowering in strength with increase in firing temperature in Al containing sample has been attributed to the decrease in the amount of Al_4C_3 phase with the increase in the firing temperature. The oxidation resistance was reported to improve with both Al (0-5wt %) as well as Si (0-5wt %) additives. However, the formation of SiO_2 layer at the surface limits the improvement in the oxidation resistance at higher percentage of Si addition. The effect of combined addition of aluminum and silicon metal powder on the performance and properties of alumina graphite composite refractories have been studied by Guoqi, **Liu.et al [9].** It has been reported that the weight loss for the sample without metal additive was less than that with metal additive, when heat-treated at same temperature. The weight loss of the sample with metal additive was found to decrease with heat treating temperature. The strength of sample with additives was higher than that without additives and was found to decrease

slowly above 1200 ˚C. The bulk density of the sample with additives was higher (lower apparent porosity) that of sample without additives which was found to increase with increase in temperature. This is due to the in-situ AlN and a little Al_4C_3 formation when heat-treated at temperature above 1200 ˚C. The formation of Al_4SiC_4 in the samples containing both the additives leads to the increase in strength when fired above 1300°C. **Shaowei et al [10]** have studied the behavior and effects of antioxidants like $Al_8B_4C_7$ and Al_4SiC_4 on the carbon containing Al_2O_3-C refractories. It has been reported that $Al_8B_4C_7$ and Al_4SiC_4 showed an excellent oxidation resistance. This is due to the fact that when $Al_8BB_4C_7$ Added to carbon-containing refractory, it reacts with $CO_{(g)}$ to form Al_2O_3 and B_2O_3 which further react with each other to form liquid phase at low temperatures. The liquid phase forms a protective layer on the surfaces of the refractory and thus inhibits the oxidation of the refractory. However, this effect of $Al_8B_4C_7$ as an antioxidant decreases at high temperature, owing to the evaporation of B_2O_3. On the other hand, Al_4SiC_4 forms protective layer (Al_2O_3-SiO_2) on the surfaces of the refractory as Al_4SiC_4 reacts with $CO_{(g)}$ and thus inhibits oxidation. **Bernard Argent B. et al [11]** have studied on the effect of additives (5% Al, 10% Si, 5% B_4C & 5% BN, 5% B_20_3, and 15% Si_3N_4) on the slag resistance of $A1_2O_3$-SiO_2-SiC-C refractories in Air. A fairly good wear resistance was observed with the predicted content of SiC in the refractory in the as-fired condition. The most effective additives were found to be Si and B_4C, whilst the most deleterious was B_2O_3 as slag resistance is concerned. These results were interpreted in terms of the thermo chemical predictions, including the variation in oxygen potential with slag attack. This study enables one to rank the refractories in order of likely resistance to attack - large amounts of liquid in the as-fired state favoring attack and reported that large amounts of SiC associated with Si additions and large amounts of BN associated with B_4C additions favored resistance to attack. Although the predictions about the order of oxidation of C and SiC were found correct for iron oxide-free slag, they were found wrong for refractories other than those with silicon-containing additions exposed to iron oxide-bearing slag. This was due to the slow rate of oxidation of SiC at low oxygen activities.

For the most effective productivity of the steel plant, these high duty refractories need to fulfil a number of demanding and partial controversial properties: high corrosion and erosion resistance, low wettability against steel- and slag-melts, high thermal shock resistance, as well as high mechanical strength and oxidation resistance at elevated temperatures. An optimization of the

above properties and thus the refractory performance can be achieved by an appropriate adjustment of their microstructure.

The main drawback in alumina graphite refractories is their oxidation at high temperatures which leads to the deterioration of properties in refractories. One of the effective means of reducing the oxidation in this type of refractories has been the use of antioxidant, Al and Si have been a popular choice with the industry because of their relative low cost and an acceptable performance. The formation of aluminum carbide and nitride phases in the Al-added samples resulted in oxidation resistance improvement in the refractory samples. In the Si added samples the formation of SiC is thought to be the major cause of improvement in the properties

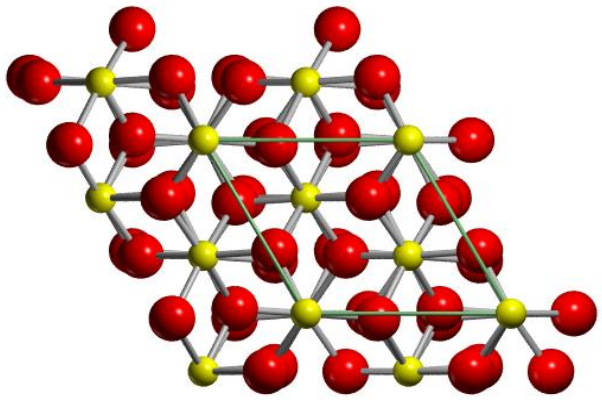

Fig 2.2: Crystal structure of Al_2O_3

2.3 Erosion or Corrosion in Al_2O_3-C slide gate plate refractory

The corrosion resistance and microstructure of Al_2O_3-C slide gate plate refractories have been studied by **Qingcai Liu et al [12]** in smelting reduction melts by the quasi-stationary immersion and rotary immersion test. They reported that the corrosion rate of the Al_2O_3-C (AC) based refractories was decreased with the addition of the graphitic carbon and ZrO_2. The corrosion of the Al_2O_3-C based refractories is caused by the interaction between melts and refractory, and the dissolution of the refractory. The corrosion rate of AC system refractories was found to increase with the iron oxide content of the melts and the temperature of the molten bath. **Zhao, L. et al [13]**

have studied the interfacial phenomena during the interaction of liquid iron and graphite/alumina mixtures. It has been reported that the carbon dissolution strongly depends on the wetting/non-wetting behavior of the refractory/molten metal interface or in the other wards the contact angle of the liquid iron-refractory interface. It has been observed that during the graphite/iron interactions, the contact angle changed from 64° at the initial state to 38° at the final state and thus showed a good wettability between iron and graphite. However, addition of different amounts of alumina into the graphite substrate caused the contact angle to increase. When the alumina in the substrate increased from 16.7 to 23.1%, the contact angle demonstrated a sharp change from good wetting to almost non-wetting. A fairy high rate of carbon dissolution was observed when the contact angle was low (at low alumina content) on the other hand it decreases sharply when the alumina in the substrate increased from 16.7 to 23.1%. This decrease rate of carbon dissolution has been attributed tothe poor wetting behavior of graphite/alumina substrate.

The interaction between slag- Al_2O_3-SiC-SiO_2-C refractory has been investigated by **Hong, Lan.et al [14].** The composition of the slag and refractory studied in this investigation were 45.4% SiO2 - 36.6% CaO - 15.9% Al_2O_3 and 69.4% Al_2O_3 - 7.3 % SiO2 - 10.6 % SiC - 12.7 % C respectively. The slag refractory interaction has been studied in the temperature range 1773 to 1873 K. XRD study confirmed that the formation of mullite when the refractory samples were maintained at high temperatures. The refractory/slag reaction has been evaluated from the carbon dissolution of the refractory. The time dependence carbon dissolution from the refractory was found to follow a two-step process. During the initial stage the carbon dissolution rate was high and then it is decreased. The high carbon dissolution from the refractory has been correlated with the evolved gases. The gas chromatographic analysis study confirmed the evolution of both CO and CO_2 gases during the initial stage however the latter disappeared as the time increased. The main in-situ reaction product was SiC rather than SiO. Slag showed a good wetting with the refractory and penetrated into the refractory through pores. The formation of low melting compounds like anorthite ($CaAl_2Si_2O_8$) and gehlenite ($Ca_2Al_2SiO_7$) were confirmed at the slag refractory interface when heated for a longer time. The role of ash impurities in the depletion of carbon from the alumina-graphite refractory into liquid iron have been investigated by **Khanna, R. et al [15]** Two natural graphite, containing 2.1% (NG_1) and 5.26% ash (NG_2) were used in this study. The carbon pick-up by liquid iron from alumina–natural graphite has been measured at 1550°C by a sessile drop arrangement and was compared with the carbon pick-up from alumina–synthetic graphite mixtures. It has been

observed that both natural graphite under investigation, showed high level of carbon dissolution into liquid iron. The presence of up to 30% alumina had negligible effect on carbon dissolution from alumina–natural graphite refractories with carbon concentration in the melt reaching 5wt%. However a significant reduction in carbon dissolution was observed for alumina in the concentration range 30 to 40wt%. Further it was observed that the significant differences in ash composition of the natural graphite used under this investigation leads to the difference in the nature of deposits observed in the interfacial region. While a small number of sporadic deposits were observed in the case of alumina–NG1 mixtures, a layer of fused ash appeared to cover the interfacial region in case of NG2. However in both cases, EDS analysis of the interfacial region indicated the presence of Ca, Mg, Al, Fe, O and S in close vicinity. It was therefore confirmed that alumina in the refractory interacts with various oxides present in the ash impurities.

Sasai, K. et al [16] have investigated the reaction kinetics between silica-containing alumina graphite refractory and low carbon molten steel. The study suggested that the rate of reaction between the refractory and the molten steel was controlled by diffusion of the SiO gas and CO gas through the pores of oxide film formed at the refractory-molten steel interface. The rate of the reaction between the refractory and the molten steel was found to be dependent on steel grade. For example the reaction was found faster in the Ti-killed molten steel than in the Al killed molten steel. This steel grade dependence had been ascribed to the differences in the gas permeability through the oxide film formed at the refractory-molten steel interface. In other words, the surface of the refractory immersed in the Al-killed molten steel was nearly covered with a relative dense oxide film present in both solid and liquid phases, whereas the surface of the refractory immersed in the Ti-killed molten steel was discontinuously covered with a relative porous oxide film in the solid phase.

2.4 Objective and approach of the present work

In the present work, the objective is to improve the thermo-mechanical properties of Al_2O_3-C slide gate plate refractories. This can be achieved by efficient microstructural design of the Al_2O_3-

C slide gate plate refractory. A specially formulated graphite (SFG) is used to partly replace the flaky graphite in the Al_2O_3-C refractory composition. SFG is a more reactive form of carbon with high surface area that can react with oxide contents and/or antioxidants to form various nano structural oxide and carbide phases. The presence and distribution of the phases are expected to improve the properties of Al_2O_3-C refractory.

Chapter 3

EXPERIMENTAL

3.1 Fabrication of Al_2O_3-C refractories

In this section the various processes followed for the fabrication of the refractory is described

3.1.1 Raw materials

Commercially available Tabular alumina, flake graphite, carbon black, specially formulated graphite (SFG), silicon metal powder were used to maintain in a pan mixture, Liquid resin and resin powder were taken as additives of base raw materials for the fabrication of alumina carbon slide gate plate refractory.

As mentioned earlier, this research work is centred on the preparation of specially formulated graphite (SFG) to use in Al_2O_3-C refractory as partial replacement of graphite.

In this present work tabular alumina of different grain size were taken, silicon powder, High purity graphite, 97 FC, was taken as a raw material, the chemical analysis of the graphite is mentioned in the Table 3.1.

Table 3.1: Chemical analysis of flake graphite:

Raw material	Carbon (%)	Volatile matter (%)	Ash (%)
Flake graphite	97.05	0.69	2.26

Novalac type resin was used as a binder. The resin had a carbon yield of ~48%. The properties are tabulated in Table 3.2.

Table 3.2: Physical and chemical analysis of liquid resin:

Properties	Liquid resin
Viscosity (CPS) at 25^oC	8500-9000
Specific gravity at 25^oC	1.23
Non-volatile matter (%)	80.10
Fixed carbon (%)	47.85
Moisture (%)	~40

3.1.2 Batch preparation

Different batches of Al_2O_3-C refractory slide gate plate were prepared by taking the same amount of Al_2O_3, resin and anti-oxidant contents. However, Different compositions of Al_2O_3-C refractory slide gate plate have been fabricated using different amounts of specially formulated graphite (SFG) as partial replacement of the natural flake graphite. In the process some portion of carbon

black + graphite has been replaced with SFG with a amount of 0.5%, 0.75% and 1% respectively which is shown in the table 3.3. in this table composition of variation batches are listed. All the variations done in the study are compared with the conventionally used Al_2O_3-C refractory slide gate plate composition prepared under similar conditions.

Table 3.3: Composition of four samples

	Composition – 1 (wt %)	Composition – 2 (wt %)	Composition - 3 (wt %)	Composition – 4 (wt %)
Tabular Alumina	92	92	92	92
Carbon Black	1.5	1.25	1.15	1
Graphite	1.5	1.25	1.15	1
S.F.G	0	0.5	0.75	1
Silicon metal	5	5	5	5
Resin	7	7	7	7

3.1.3 Mixing and aging

The purpose of mixing the raw materials is to make a refractory batch and transform all the solid components and the liquid additions into a macro homogeneous mixture that can be subsequently shaped by one of the numerous fabrication methods employed by modern refractory manufacturers. All the above batches were separately mixed in a pan mixer at room temperature for a period of 45 minutes. All the solid raw materials and liquid additives are mixed in a sequence to get a macro homogeneous mixture.

After mixing of the materials, the batches were kept for 24 hours for ageing. During aging the polymerization of resin takes place by developing carbon-carbon bonds in resin. Subsequently the matrix was compacted to give a desired shape by pressing.

3.1.4 Pressing

The mixed materials after aging were compacted to give a desired shape by pressing. The aged mixtures were pressed uniaxially by hydraulic press in a steel mold the face pressure of 2000kg/cm^2. An appropriate weight of each mixture was taken to get the desired green density and the size of the slide gate plate. The steel mold was cleaned using cotton and brush after each pressing. The mixtures were charged slowly into the mold cavity and leveled uniformly in order to avoid lamination in the pressed slide gate plate.

3.1.5 Tempering

Tempering is the heat treatment process of the refractories at low temperature to remove volatile matters from the organic green binders and to impart enough green strength for handling. By this process the chemical bond is developed in the refractory grains and the bonding phase. Tempering of the pressed green bricks was done at 200^{o}C for 24 hours. With the increase in temperature phenolic resin got converted to carbonaceous phase which helped in developing a stronger carbonaceous bond for the refractory brick and increased mechanical strength of the brick.

3.1.6 Coking

After tempering the bricks were cut into different pieces having different sizes for the purpose of different testing. Coking was carried out at 1050^{o}C for 4h under reducing atmosphere. Subsequently, piece of the refractory specimens were coked at 1350 °C for 4 hours under reducing atmosphere to characterize microstructure.

3.2 Characterization

3.2.1 Apparent porosity (AP)

Apparent porosity is the percentage relationship between the volume of the open pore space and the total volume of the sample. It is the ratio of total volume of the close pore to its bulk volume, close porosity is the Closed porosity is the pores that are not penetrated by the immersion of liquid, whereas open porosity are those pores which are penetrated by the immersion liquid, The AP and BD were measured by the Archimedean principle.

The test samples were cut from the cooked slide gate plate. After taking dry weight all the samples were put into a container and water was added. Then the container was heated for 2 hrs. So that all the open pores are filled with water. After that, the suspended weight (W_2) and soaked weight (W_3) were taken and AP was calculated as follows:

$$AP = (W_3-W_1) / (W_3-W_2) \times 100$$

3.2.2 Bulk density (BD)

BD is the ratio of the mass of the dry material of a porous body to its bulk volume expressed in gm/cm^3 or kg/m^3, where bulk volume is the sum of the volumes of the solid material, the open pores and the closed pores in a porous body. BD was measured of the coked sample.

Whereas true density is the ratio of mass of the material of a porous body to its true volume and true volume is the volume of solid material in a porous body.

$$B.D = (W_1/W_3\text{-}W_2) \times \text{density of liquid at temperature of test}$$

3.2.3 Cold crushing strength (CCS)

Cold crushing strength of refractory can be measured by placing the sample on the flat surface by the application of uniform load to it by a hydraulic compression testing machine. The load at which cracks appear in the refractory sample represents the CCS of the sample. The test samples were cut from the standard slide gate plate samples. The load is applied uniformly on the sample in the flat position. It is expressed as kg/cm^2.

The ccs can be calculated by,

$$CCS = \text{Load/Area } (kg/cm^2)$$

3.2.4 Hot modolus of rupture(HMOR)

The modulus of rupture of refractory specimen is determined as the amount of force applied to a rectangular test piece of specific dimensions until failure occurs. This test method covers the determination of the modulus of rupture of carbon-containing refractories at elevated temperatures in air. Each value of HMOR was the average of two parallel specimens. It was done by three - point bending test using HMOR testing apparatus. All the specimens for HMOR were taken as 150mm × 25 mm × 25 mm without pre-firing at air atmosphere. The final temperature of HMOR was 1400^{o}C with a heating rate of heating rate of 5^{o}C/min. It was done in air atmosphere with a soaking time of 30 min. Finally, the loading rate of HMOR was 1.2-1.4 kg/s according to samples.

The HMOR value was calculated by the following formula:

$$HMOR = (3W \times L) / (2b \times d^2)$$

Where “W” (kg) is the maximum load when the specimen is broken; “L” is the span length between the lower supporting points. (125 mm for all the tests in the work); “b” is the breadth (cm), “d” is the height of the specimen (cm)

3.2.5 Oxidation resistance

Oxidation resistance of the fabricated bricks was tested on cube shaped samples. The samples were fired in an electrical furnace at 1400^{o}C for 5 hours in air atmosphere. At this temperature all the carbonaceous materials of the brick got oxidized particularly from the outer surface. The colour of the oxidized portion turned off-white compared to the black colour of the virgin brick and therefore the boundary between the un-oxidized and the oxidized regions were quite evident. After the heat-treatment, the cuboid shaped samples were cut and the diameter of black portion was measured at different locations and the average value was taken. Lower oxidation index indicates the higher oxidation resistance of the brick

Oxidation index is determined by the formula: Oxidation index = (Area of oxidized zone / Total area) × 100.

3.2.6 Phase and microstructural analysis

Microstructures of natural flake graphite, SFG were studied using standard Scanning Electron Microscopes (NOVA NANO-SEM). The accelerating voltage was 15/20 kV. The powders were fixed on a self-adhesive carbon tape. For micro-structural analysis of Al_2O_3-C samples we cut thin pieces from the slide gate plate. Then those thin slices of samples were observed through electron microscope.

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Chapter 4

RESULTS & DISCUSSIONS

4.1 Analysis of special additive

The physical study of natural graphite was done by using different experimental techniques like FESEM, XRD. Natural graphite were characterized from the points of view of their particle size, crystallinity, purity etc.

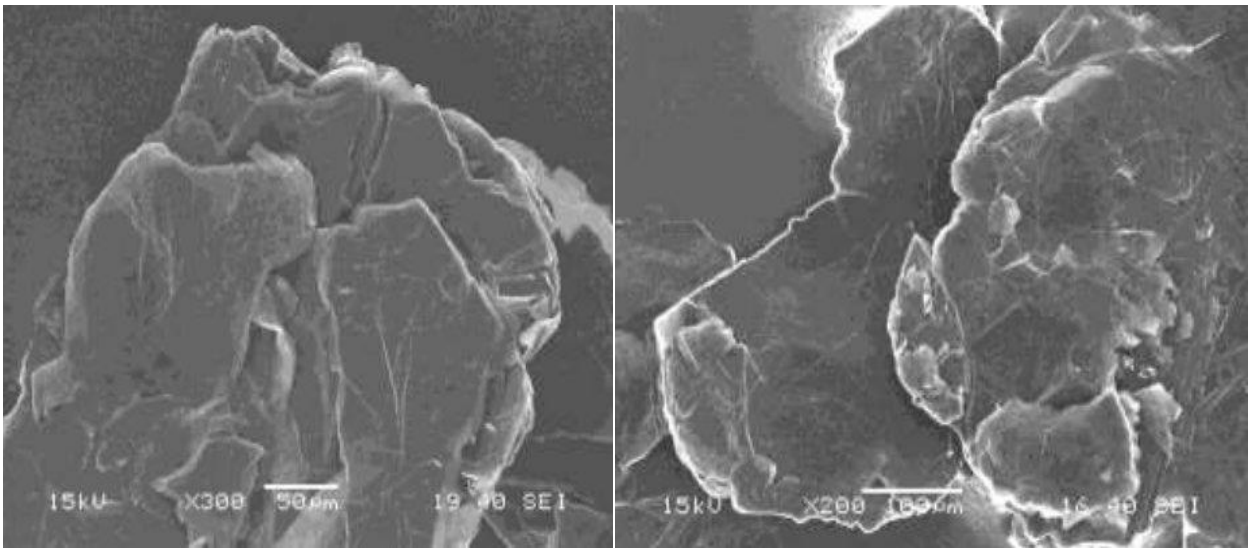

Fig 4.1: FESEM images of natural graphite

The natural graphite is flaky in nature and the graphene layers are attached together was observed by FESEM Fig 4.1. From the FESEM images it was also observed that the dimension of graphite flakes is more than 200 µm.

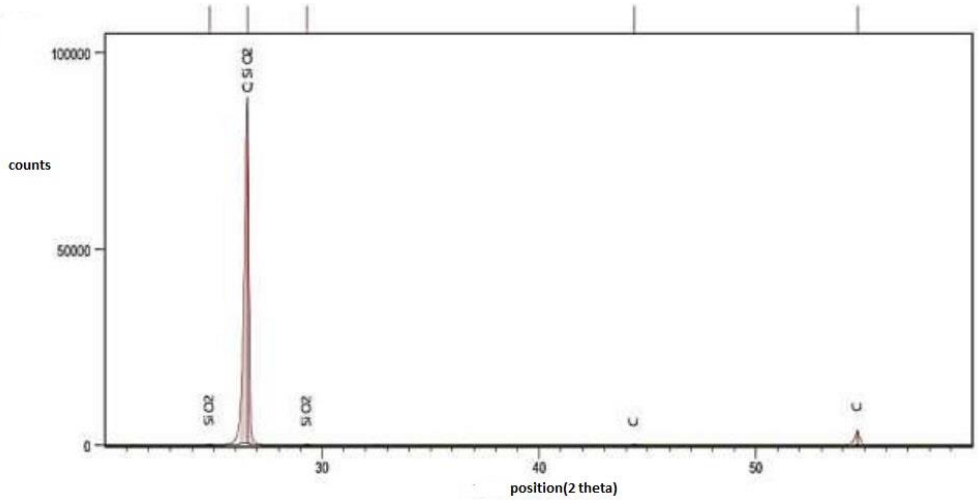

Fig 4.2: XRD pattern of natural graphite

From the fig 4.2 the XRD pattern can be seen that there was some silica impurities present already in the natural graphite. The peaks at 26.56^{o} and 54.69^{o} is consistent with the (002) and (004) peaks of graphite respectively.

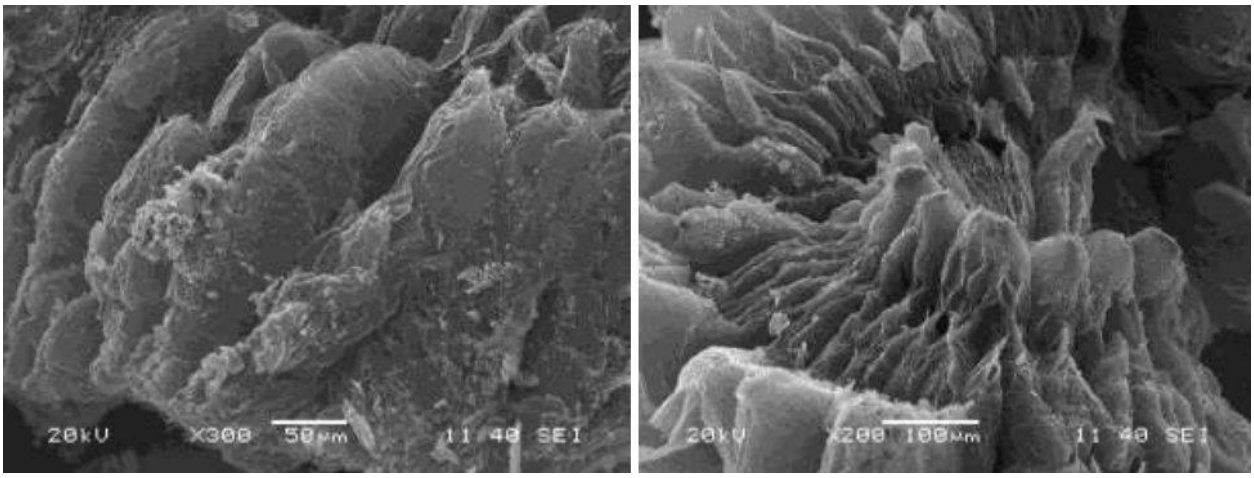

Fig 4.3: FESEM images of specially formulated graphite (SFG)

From the fig 4.3 the FESEM images of specially formulated graphite it was clearly visible that the natural graphite has converted to a highly porous and low density material based on the available surface area, these form of graphiteis expected to be highly reactive in nature

Table4.1: Weight percentage of carbon, hydrogen & nitrogen in specially formulated graphite

Sample name	Carbon (%)	Hydrogen (%)	Nitrogen (%)
Exfoliated graphite	73.56	4.47	2.14

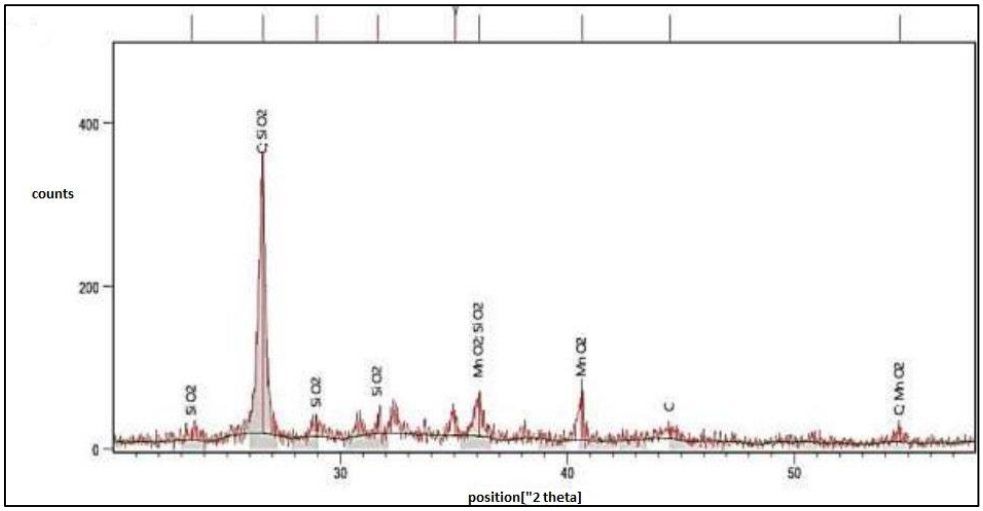

Fig 4.4: XRD pattern of specially formulated graphite (SFG)

In the fig 4.4 the XRD pattern of specially formulated graphite is similar to the natural graphite except some extra impurity peaks which may have come due to manganese oxide. There's difference in the peak intensities. Natural graphite shows a sharp and symmetric peak shape because of its high crystallinity. On the other hand, SFG exhibits much reduced intensity of the (002) peak, indicating fine crystallites of graphite (in thickness dimension)

4.2 Physical properties

4.2.1 Apparent porosity

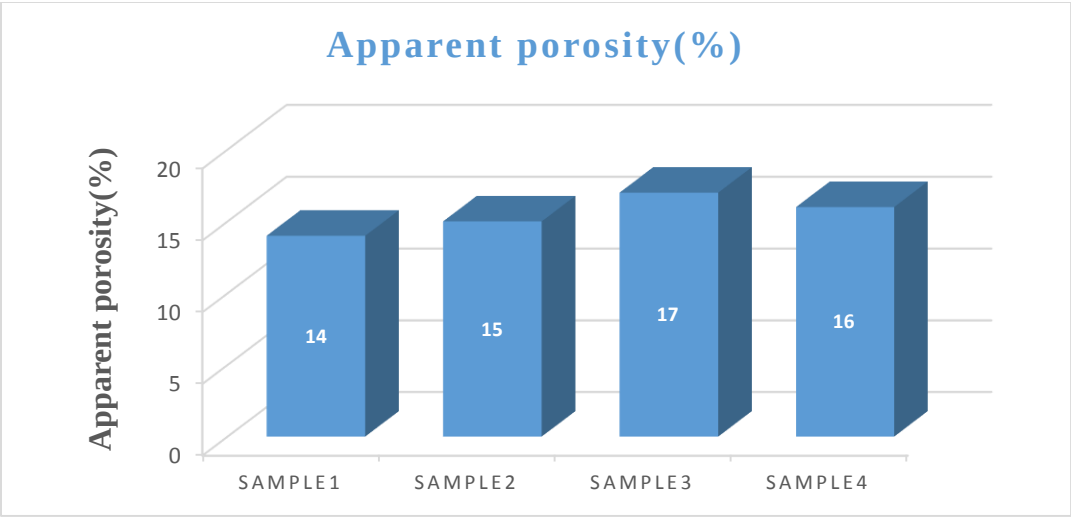

Fig 4.5: Variation of apparent porosity with specially formulated graphite content

Apparent porosity is the percentage relationship between the volume of the open pore space and the total volume of the sample. The change in AP with the increase of SFG is shown fig 4.5. With the addition of SFG the percentage of AP is increasing due the defect in mixing process, however, the variation is only in sample3. But in sample 3 exhibited 3% increase in AP, which is due to improper mixing or pressing process

4.2.2 Bulk density

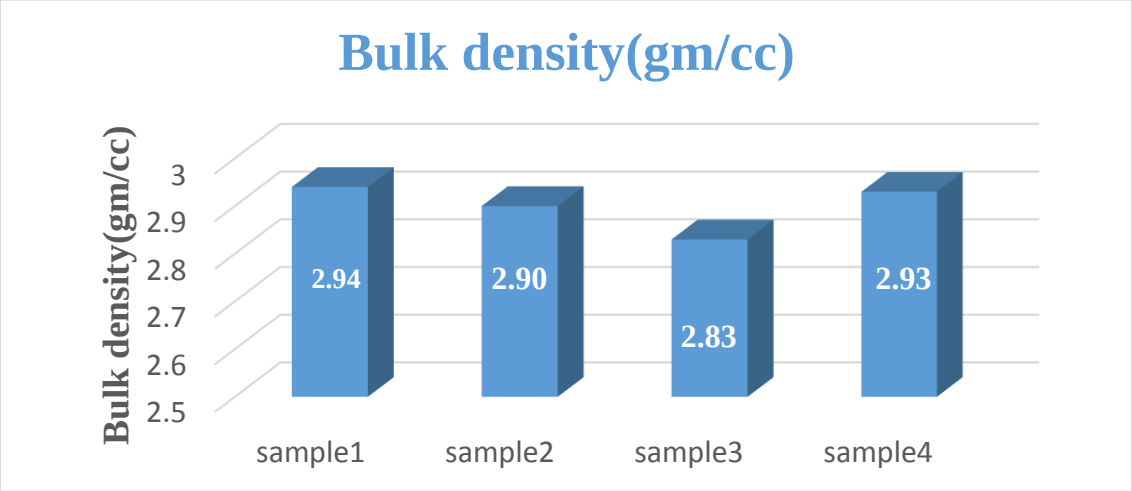

Fig 4.6 Variation of bulk density with specially formulated graphite content

Bulk density is the weight per unit volume of the refractory including the volume of open pore space. We have observed bulk density decreases with increase in amount of specially formulated graphite.as SFG forms SiC fibers. But at 1% SFG having sample4 that increase in density and amount of SiC fibers which is shown in fig 4.6.

4.3 Cold crushing strength

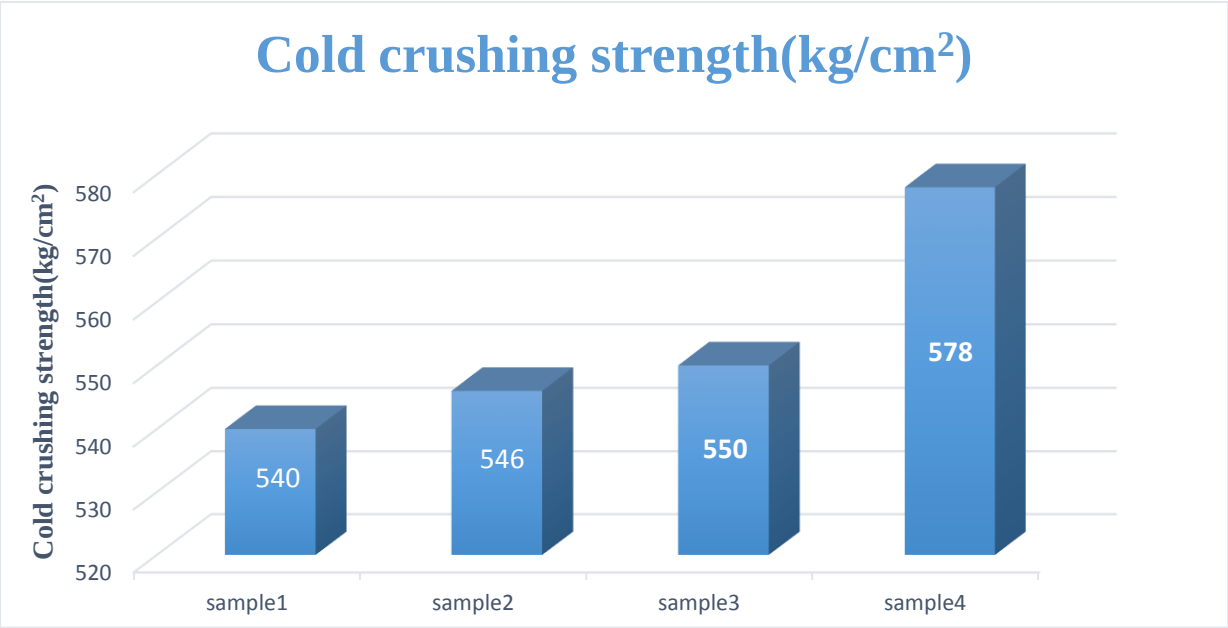

Fig 4.7: Variation of cold crushing strength with specially formulated graphite content

Cold crushing strength of the refractories is carried out by placing a suitable refractory specimen on a flat surface followed by application of a uniform load to it through bearing block in a standard mechanical or hydraulic compression testing machine. The load at which cracks appear in the refractory specimen represents the CCS of the specimen. The variation of cold crushing strength with the SFG is shown in fig4.7. From the figure it is clear that with the increase of SFG cold crushing strength increases. The CCS value of the sample which contains no SFG is 540 kg/cm^2 but for sample4 CCS value is 578 kg/cm^2. The cold crushing strength properties showed 7.03% increase as compare to the industrial standard. Increase in CCS is because of the increase of SFG which causes better filling of pores and results in an increase in BD. But for sample4 best pore filling is achieved. So, further addition of SFG does not affect the CCS value much.

4.4 Hot modulus of rupture

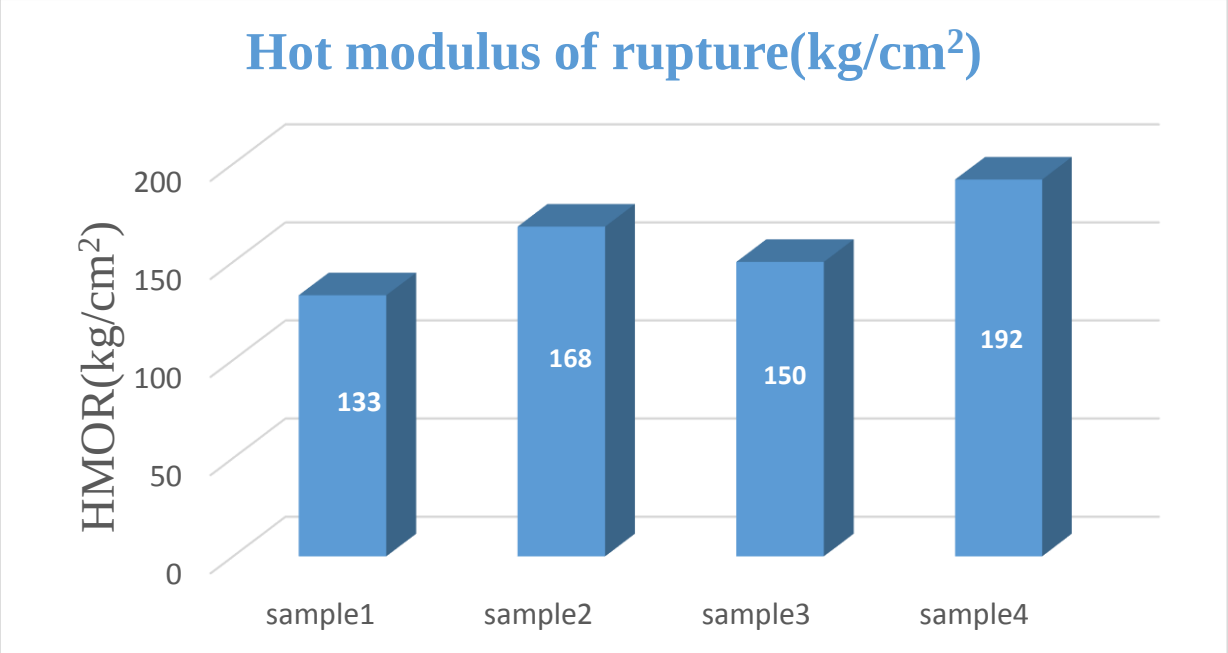

Fig 4.8: Variation of hot modulus of rupture with specially formulated graphite content

. From the figure 4.8 it is clear that with the increase of SFG hot modulus of rupture increases. The HMOR value of the sample which contains no SFG is 133 kg/cm^2 but for sample4 HMOR value is 192 kg/cm^2. Hot strength showed 44.36% increase as compared to that of the industrial standard. With the increase of SFG pores inside the bricks fill better. So, the strength of the bricks enhances. Because of high surface area, SFG is more reactive than graphite. So, at the high temperature, higher amount of carbide forms by reacting with antioxidants with the increase in SFG. Hot strength showed 44.36% increase as compared to that of the industrial standard.

4.5 Oxidation resistance

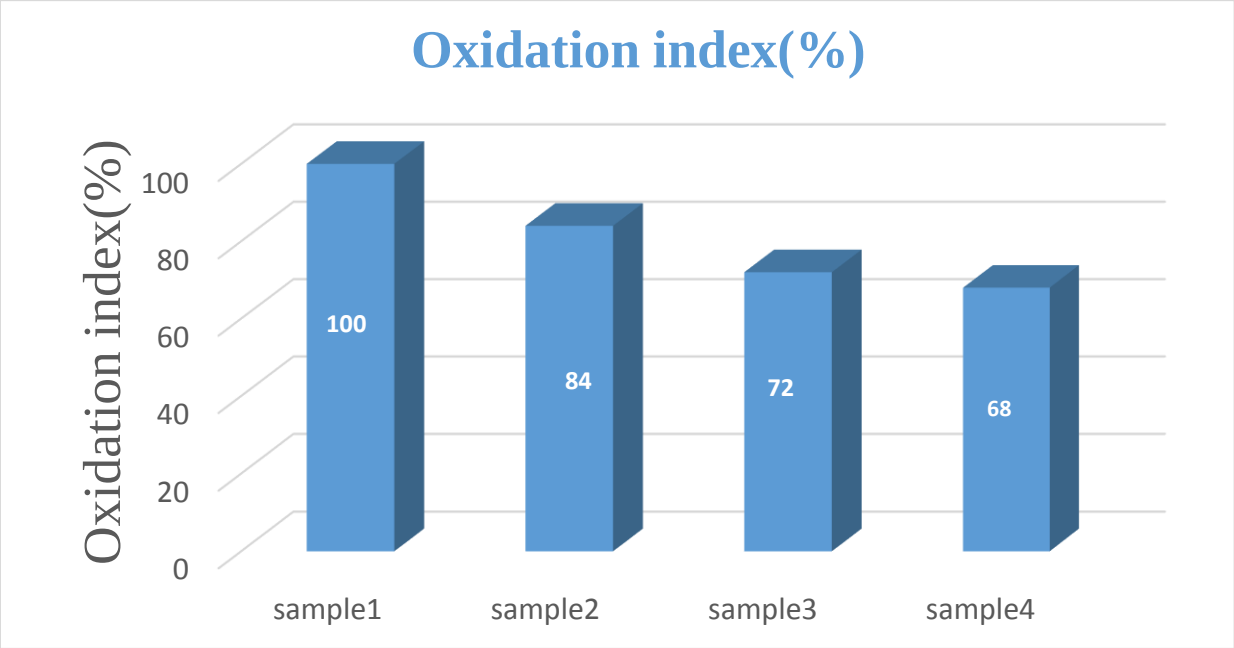

Fig 4.9: Variation of oxidation index with the variation of specially formulated graphite content

From the fig 4.9 it is clear that with the increase of SFG oxidation resistance increases. The oxidation index values decrease with increase in SFG from 100% to 68%. Oxidation index calculated from oxidized area of the refractory, indicates 47.05% decrease which is an outstanding result. As SFG forms carbide which has higher oxidation resistance property than that of natural graphite so, the oxidation index decreases with the increase of specially formulated graphite (SFG).

4.6 Microstructural analysis of the composite by SEM and XRD

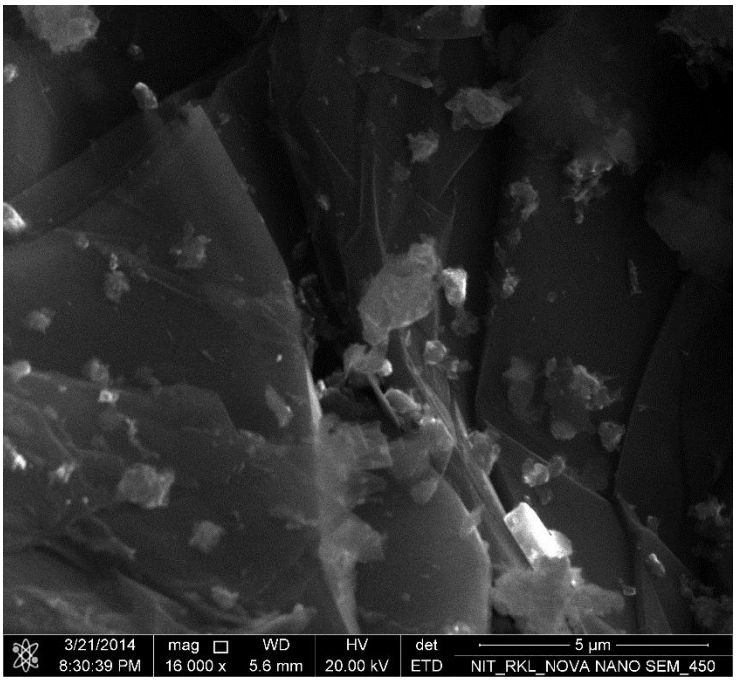

Fig 4.10: FESEM of sample1

In fig 4.10 Sample1 (Al_20_3-C):- In this sample as SFG is not added so it did not form SiC fibers. As we have found sample2, sample3, sample4 containing SFG. Due to which oxidation resistance and cold crushing strength, and hot modulus of rupture is low.

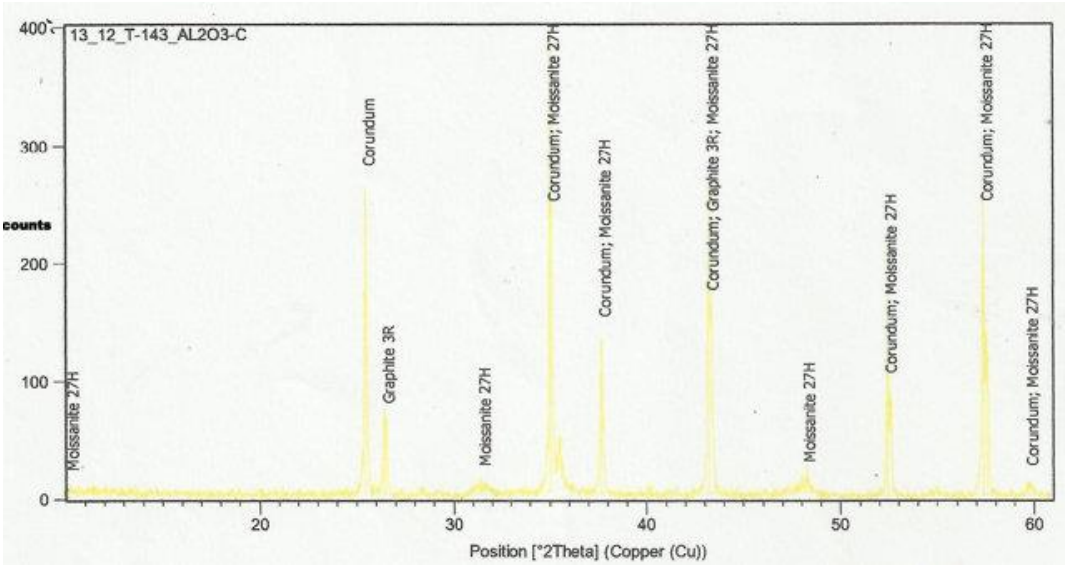

Fig 4.11: XRD of sample1 (Al_2O_3-C)

In fig 4.11 the XRD pattern of samples shows that the formation of different phases like graphite 3R but only a small amount of SiC has formed in the sample1 that has no SFG. Which means it is having less CCS, HMOR, oxidation index as compare to other 3 samples.

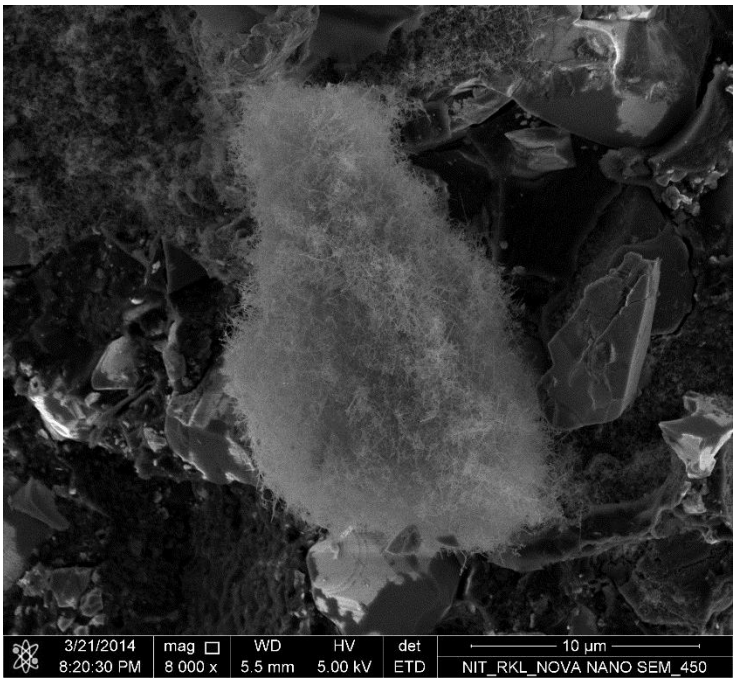

Fig 4.12: FESEM of sample 2

In fig 4.12 Sample 2 (Al_20_3-C +0.50% EG):- It showed better oxidation resistance and cold crushing strength, and hot modulus than the sample1 (Al_20_3-C) in the second sample these localized formation of SiC carbide fibers which gives batter properties then sample1 (Al_20_3-C). But sample2 properties are inferior then sample3 as sample3 contain 0.25% more SFG then sample 2. As a result it produce more Sic fibers hence so batter properties. The SiC fibers are not forming equally the above SEM we seen that the lumping of SiC in some selected parts of the sample.

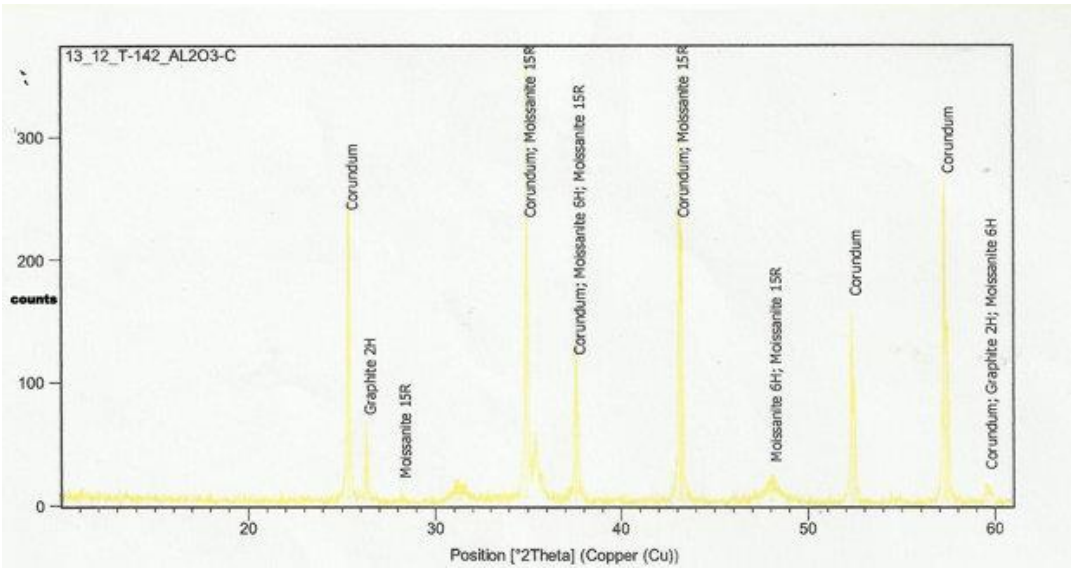

Fig 4.13: XRD of sample 2 (Al_2O_3-C+ 0.50% SFG)

In fig 4.13 the XRD pattern of samples shows that the formation of different phases like graphite 2H, moissanite 15R, moissanite 6H. But the addition of SFG a different phase of SiC are shown in the above XRD that is moissanite 6H which initiates the forming of SiC fibers. Due to which the mechanical strength of sample 2 is better than sample 1.

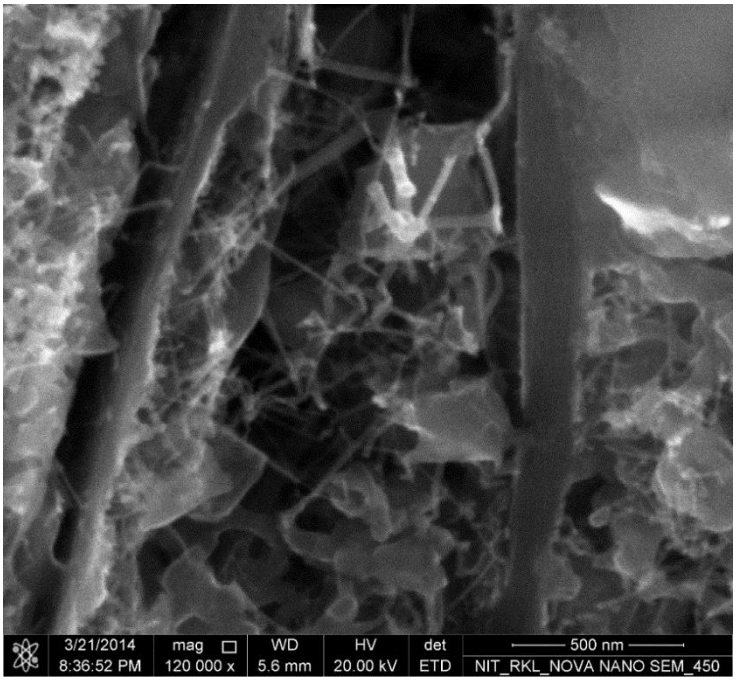

Fig 4.14: FESEM of sample 3

In fig 4.14 Sample3 (Al_2O_3-C+0.75%SFG):- From the FESEM image we have observed the formation of SiC fibers within the interparticular porosity This SiC fibers act as a crack bridger increasing the fracture toughness of the sample. So we conclude that from the above FESEM by the addition of more 0.25% of SFG the SiC fibers are increases and it helps in bridging the cracks which increases strength and resist the deformation of the sample.

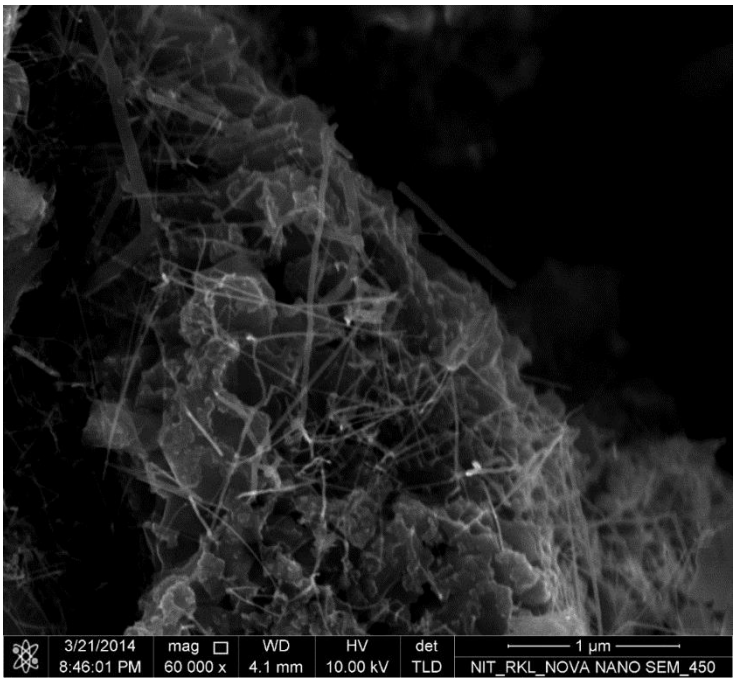

Fig 4.15: FESEM of sample 4

In fig 4.15 Sample4 (Al_2O_3-C+1%SFG):- It contain highest amount of SFG so hence there is uniform distribution of SiC fibers throughout the sample. Which results in the best cold crushing strength, hot modulus of rupture and oxidation resistance. From the above fig 14 we conclude that by the addition of 1% SFG the SiC fibers are highest and it was distributed all over the sample equally so that the thermo mechanical strength, HMOR, CCS, oxidation resistance shows the best result among the four samples.

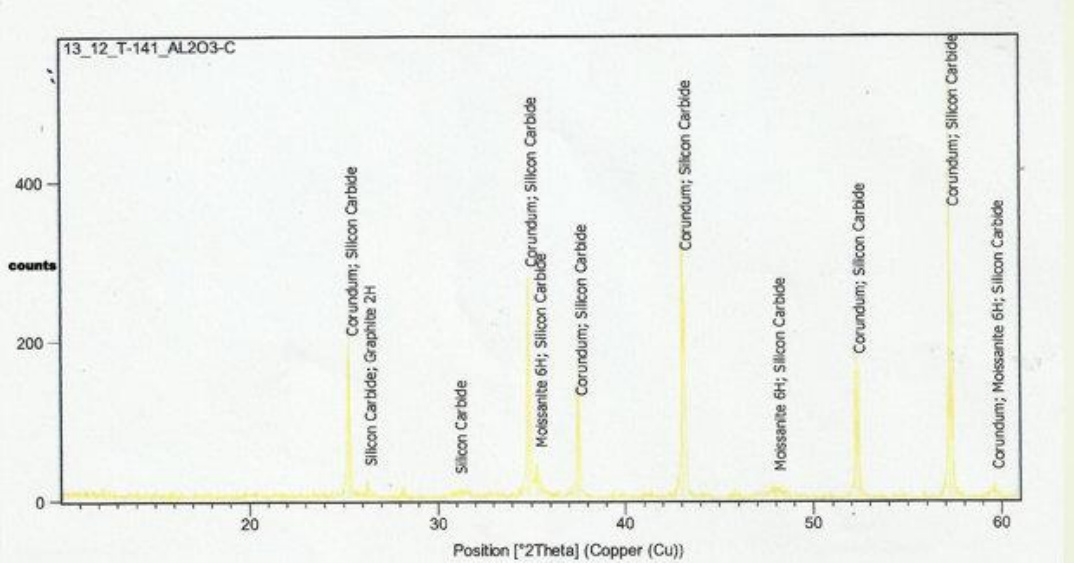

Fig 4.16: XRD of sample4 (Al_2O_3-C+ 1% SFG)

In fig4.16 the XRD pattern of samples shows that the formation of different phases like silicon carbide, graphite 2H and moissanite 6H. By the addition of 1% of SFG direct SiC fibers are forming which were not seen in any above 3 of the samples, this result the best sample which provide good thermo mechanical strength, high HMOR, high CCS and high oxidation resistance.

In the XRD, sample4 SFG showed formation of SiC fibers and the amount of fiber increases with increase in amount of expanded graphite. As sample1 does not contain any SFG so it does not show any SiC fibers.

Chapter 5

CONCLUSION

An attempt has made to reduce the carbon content of the Al_2O_3-C slide gate plate refractory by replacing a part of graphite by the specially formulated graphite (SFG) in this study.The total carbon used in this refractory is 3%. Other raw materials used for this study were tabular alumina antioxidants (Si power) and resin as binder (both liquid and powder) and hexamine. The compositions were mixed and pressed and then various refractory properties were measured. The effect of specially formulated graphite was studied by different characteristics of the refractory and the properties were compared with the refractory which contained no specially formulated graphite under similar manufacturing conditions.

The significant features of the new class of refractories fabricated are shown below.

i. The newly fabricated Al_2O_3-C refractories exhibited only small little variation in apparent porosity. As compared to the standard Al_2O_3-C refractory (with no SFG).
ii. Trends similar to AP were observed with regards to BD of the refractories, which is trivial.
iii. The new compositions exhibited a maximum of ~7% increase in the cold crushing strength relative to the standard compositions
iv. Two of the new compositions exhibited phenomenal increase in HMOR. The increment was almost 44 higher than that of the standard Al_2O_3-C refractory.
v. Dramatic increase in oxidation resistance was observed for the new compositions with an index of ~68% as compared to ~100% for the standard composition.
vi. Refractory specimens coked at 1050 C exhibited much better formation of SiC particles in the SFG added refractories as compared to the standard specimen.
vii. Scanning electron micrographs of the coked samples exhibited formation of SiC nanowires throughout the refractory interparticular space in the SFG based compositions. The extent of SiC formation was considerably lower in the standard refractory without any SFG.
viii. The SiC nanowires crisscrossed throughout the refractory body, which prevented oxidation. These fibers also acted as crack bridging elements, and consequently the hot strength of the refractory increased.

In totally we have formulated a low carbon Al_2O_3-C refractory with 3% graphite with special carbon additives that exhibits excellent thermo-mechanical properties as noted above.

Three of the compositions sample2 and sample3 had either comparable or inferior properties as compared to the standard composition. On the other hand, sample4 exhibited dramatically improved thermo-mechanical properties including HMOR, oxidation resistance.

The technology demonstrated in this work is generic to carbon/graphite containing refractories in that many of this class of refractories can be strengthened with this approach. This opens up great opportunities to explore new and improved refractory systems.

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